

Theory of flexoelectric effect in crystals

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The linear response of polarization to a strain gradient is examined. It is shown that it is possible to distinguish four contributions of different physical origin to this effect, namely, two bulk and two surface contributions. A microscopic theory is developed for the bulk contributions, using the rigid-ion approximation, and a phenomenological description is developed. It is shown that the bulk effect is different for static inhomogeneous strain and a propagating sound wave. The magnitude of the effect is estimated for the surface contribution. It is shown that the bulk and surface contributions are of comparable order of magnitude. The feasibility of an experimental investigation of the effect in ordinary dielectrics and ferroelectrics is discussed.

1. INTRODUCTION

The flexoelectric effect consists of the appearance in an inhomogeneously deformed body of dielectric polarization proportional to the strain gradient. This phenomenon was first predicted theoretically by Mashkevich and Tolpygo,^{1,2} who studied the long-wave lattice dynamics of crystals with diamond structure. A phenomenological description of the effect was proposed by Kogan.³ It effectively takes into account terms of the form

$$f_{\alpha\beta\gamma\delta} P_{\alpha} \frac{\partial w_{\beta}}{\partial x_{\gamma} \partial x_{\delta}} \quad (1)$$

in the free energy density, where \mathbf{w} is the displacement vector and \mathbf{P} is the polarization.¹⁾ The symmetry of the tensor \hat{f} was analyzed by Indenbom, Loginov, and Osipov.⁴

Although the flexoelectric effect is possible in crystals of any symmetry, there is particular interest in centrosymmetric crystals that do not exhibit the piezoelectric effect. Thus, the flexoelectric effect plays an important role in the description of the interaction between elastic strain and free electrons in a nonpiezoelectric crystal. According to the estimates reported by Tolpygo² and Kogan,³ the flexoelectric effect and the strain potential ensure the same order of magnitude for the interaction energy between an acoustic wave and free carriers.

Until now, it has always been implicitly assumed in discussions of the flexoelectric effect that its "general properties" are analogous to the properties of the piezoelectric effect. In particular, it is considered that: (1) under the same macroscopic electrodynamic conditions, the effect manifests itself in the same way in statics and dynamics, i.e., under the conditions of inhomogeneous static strain and propagating acoustic wave and (2) the effect is essentially a bulk effect, i.e., when it is determined from changes in the total polarization of a finite specimen under homogeneous strain, the surface contribution is small in the parameter d/L (d is the thickness of the disturbed surface layer and L is the smallest of the characteristic linear dimensions of the specimen).²⁾

In this paper, we discuss the flexoelectric effect in detail and show that it does not exhibit any of these properties. In particular: (1) the proportionality factor between polariza-

tion and the strain gradient is different in a propagating wave and in static inhomogeneous strain, where, in general, the difference is of the order of these quantities themselves and (2) under inhomogeneous strain of the crystal, the surface contribution to the average dipole-moment density, evaluated for the specimen as a whole, may turn out to be of the order of the bulk contribution. We shall also discuss the properties of the piezoelectric effect in pyroelectrics, since this question turns out to be fundamentally related to the surface contribution to the flexoelectric effect.

Our results are in conflict with the results reported on the flexoelectric effect in Ref. 4, and with the work of Born and Huang⁶ and Martin⁷ on the piezoelectric effect in pyroelectrics. The reasons for this discrepancy will be discussed below.

Section 2 is devoted to the phenomenological description of the flexoelectric effect. Section 3 and the Appendix give a solution for the response of optical displacements to a strain gradient. Section 4 uses the results of Section 3 to obtain a microscopic expression for the phenomenological parameters introduced in Section 2 in the description of the flexoelectric effect. Section 4 also analyzes the piezoelectric and flexoelectric response to a spatially uniform perturbation in a finite specimen, and provides a more precise definition of the flexoelectric effect together with a discussion of the surface contribution to it. Section 5 reviews all these results in the case of an ordinary dielectric and a ferroelectric. It also gives a critical review of Ref. 4.

2. PHENOMENOLOGICAL DESCRIPTION

One of the manifestations of the flexoelectric effect is that an acoustic wave propagating in a crystal of any symmetry is accompanied by a polarization wave whose amplitude is proportional to that of the strain-gradient wave. Simple phenomenological considerations can be used to verify that the proportionality factor between the polarization and the strain gradient is different for the sound wave and the stationary strain gradient. Actually, the symmetry of any crystal enables us to include not only the terms (1) in the expression for the free energy density, but also the additional term

$$\mu_{\alpha\beta} \dot{P}_{\alpha} \dot{w}_{\beta} \quad (2)$$

in the phenomenological expression for the kinetic energy density. Inclusion of the additional terms (1) and (2) in the phenomenological expression for the density of the Lagrangian leads to the following equations of motion for the acoustic displacements and polarization:

$$\rho \ddot{w}_\alpha = c_{\alpha\beta\gamma\delta} \frac{\partial^2 w_\gamma}{\partial x_\beta \partial x_\delta} - \mu_{\beta\alpha} \dot{P}_\beta - f_{\beta\alpha\gamma\delta} \frac{\partial^2 P_\beta}{\partial x_\gamma \partial x_\delta}, \quad (3)$$

$$\chi_{\alpha\beta}^{-1} P_\beta = E_\alpha - f_{\alpha\beta\gamma\delta} \frac{\partial^2 w_\beta}{\partial x_\gamma \partial x_\delta} - \mu_{\alpha\beta} \dot{w}_\beta, \quad (4)$$

where \mathbf{E} is the macroscopic electric field, $\hat{\chi}$ is the permittivity tensor, \hat{c} is the tensor of elastic moduli, and ρ is the density.

Analysis of (3) and (4) will readily show that the relationship between polarization and strain gradient is different in the case of static strain and an acoustic wave. In the former case, the two are related by the tensor $\chi_{\alpha\beta} f_{\beta\delta\gamma\eta}$ and, in the second, by $\chi_{\alpha\beta} (f_{\beta\delta\gamma\eta} + \mu_{\beta\xi} c_{\xi\gamma\delta\eta} / \rho)$. The contribution due to the tensor f will be called the bulk static flexoelectric effect and the additional contribution that appears in the dynamic situation (related to the tensor $\hat{\mu}$) will be called the dynamic flexoelectric effect. We shall show that these two contributions are of the same order in the case of the sound wave. If we start with the fact that the contribution of the off-diagonal part of the kinetic energy (2) should, in general, be of the same order as its usual diagonal part, we find that the order of magnitude estimate for the components of the tensor μ is $\mu \sim M/e$, where M is the average mass of an atom in the crystal and e is the electron charge. If we combine this with the standard estimate $c \sim e^2/a^4$, $\rho \sim M/a^3$ (a is the characteristic atomic separation), we find that $\mu c / \rho \sim e/a$. On the other hand, $f \sim e/a$ (Refs. 1–4). We thus see that the two contributions are, in fact, of the same order in this case.

Within the framework of the proposed phenomenological scheme, the flexoelectric response in the static and dynamic situations may be essentially different.

It is readily seen that the above discussion is based on the assumption that the tensor $\hat{\mu}$ differs from zero. At first sight, this is a surprising assumption in view of the fact that the diagonal form of the kinetic energy is employed in microscopic calculations. Let us examine this apparent contradiction.

Microscopic calculations commonly employ the Jacobi coordinates (see, for example, Ref. 8) and the coordinate of the center of gravity of a unit cell is identified in the long-wave limit with the acoustic displacement vector \mathbf{w} . The microscopic potential energy density of the crystal, looked upon as a function of the normal phonon coordinates \mathbf{P} and space derivatives of \mathbf{w} and \mathbf{P} then turns out to depend formally on the distribution of the masses of the atoms in the unit cell. It is clear that the introduction of potential energy that depends on the mass distribution is incorrect. However, this error does not show up in the lowest orders in spatial dispersion: the elastic constants and piezoelectric moduli calculated in the classical approximation using this potential energy do not depend on the mass distribution. However, when the flexoelectric response is calculated, the error does show up because the static flexoelectric coefficient is found to depend

on this distribution. It follows that, when the flexoelectric effect is described, we can no longer identify \mathbf{w} with the position of the center of gravity of the cell and \mathbf{w} must, in fact, be redefined so that the physically meaningless dependence of the static potential on the mass distribution is removed. It is clear that this redefinition will, in general, mean that the kinetic energy will no longer be diagonal, so that the appearance of the off-diagonal term (2) in the phenomenological expression for the kinetic energy density is perfectly understandable. Henceforth, our microscopic description will not rely on the use of transformations of coordinates that depend on the mass distribution in the unit cell, so that we shall automatically obtain an expression for the tensor \hat{f} that will be independent of the mass distribution, whilst the expression for $\hat{\mu}$ will depend on this distribution.

The above phenomenological scheme describes the bulk effect. However, when the polarization response to a constant strain gradient in a finite specimen is examined, we have to take into account surface as well as bulk contributions. It is known that the surface contributions are small in the case of the piezoelectric effect,⁵ but this is not so in the flexoelectric effect, for which there are, in fact, two essential surface contributions.

One of these contributions is due to a surface piezoelectric effect, i.e., a piezoelectric effect in the thin surface layer in which the lattice is distorted by the presence of the surface. It turns out that this can simulate the flexoelectric effect. Since this contribution can be reduced to another effect, it will be of no interest in the present context, and we shall limit ourselves to a brief analysis of it when we discuss the final results.

The second contribution cannot be reduced to other effects and, at first sight, it is not obvious that it must appear. We shall not formulate a rigorous phenomenological scheme for its description, and will limit ourselves to showing that this contribution must appear. We shall then estimate it and explain it qualitatively (see the end of Section 4).

3. OPTICAL DISPLACEMENTS IN AN INHOMOGENEOUSLY DEFORMED CRYSTAL LATTICE

The aim of this section is to find the displacements within the unit cell in an inhomogeneously deformed crystal when these displacements are proportional to the strain gradient. We shall start with the equations for the displacements $r_{\alpha p}^n$ of atoms from their respective equilibrium positions (\mathbf{n} is the lattice vector, p is the number of an atom in the unit cell, and α is the Cartesian coordinate):

$$m_p \ddot{r}_{\alpha p}^n = -\Phi_{\alpha p, \alpha' p'}^{nn'} r_{\alpha' p'}^{n'}, \quad (5)$$

where m_p is the mass of the p th atom and $\hat{\Phi}$ is the short-range part of the matrix of force constants. The contribution to $\hat{\Phi}$ of the long-range part of the dipole-dipole interaction will be taken into account, whenever necessary, within the framework of macroscopic electrodynamics.

We are interested in only the long-wave acoustic solutions of (5), and will assume that the wave vector \mathbf{K} satisfies the inequalities $L \gg K^{-1} \gg a$. Born and Huang⁶ investigated only the elastic and piezoelectric properties of the lattice,

i.e., they confined their attention to the solution of (5) in the first order in Ka , and then wrote down the condition for the correction of order $(Ka)^2$. We are interested in the response to the strain gradient, and will therefore have to find the solution in the next order in Ka . We shall repeat the set of iteration equations obtained in Ref. 6, and then provide a resumé of the analysis of these equations given in Ref. 6, since both will be useful in the discussion of our results.

It was shown by Born and Huang⁶ that, if we seek the acoustic solution of (2) in the form

$$r_{\alpha p}^n = U_{\alpha p} \exp[i\mathbf{K} \cdot (\mathbf{n} + \mathbf{x}_p) - i\omega t] \quad (6)$$

(\mathbf{x}_p is the radius vector of the p th atom in the unit cell), the contributions $\mathbf{U}_p^{(0)}$, $\mathbf{U}_p^{(1)}$, and $\mathbf{U}_p^{(2)}$ to \mathbf{U}_p in the zeroth, first, and second orders in Ka , respectively, can be found from the following set of iteration equations:

$$A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'}^{(0)} = 0, \quad (7)$$

$$A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'}^{(1)} = -iK_{\beta} A_{\alpha p, \alpha' p'}^{(1)\beta} U_{\alpha' p'}^{(0)}, \quad (8)$$

$$A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'}^{(2)} = -iK_{\beta} A_{\alpha p, \alpha' p'}^{(1)\beta} U_{\alpha' p'}^{(1)} - \frac{K_{\beta} K_{\gamma}}{2} A_{\alpha p, \alpha' p'}^{(2)\beta\gamma} U_{\alpha' p'}^{(0)} + \omega^2 m_p U_{\alpha p}^{(0)}, \quad (9)$$

where

$$A_{\alpha p, \alpha' p'}^{(0)} = \sum_{\mathbf{n}'} \Phi_{\alpha p, \alpha' p'}^{\mathbf{nn}'},$$

$$A_{\alpha p, \alpha' p'}^{(1)\beta} = \sum_{\mathbf{n}'} \Phi_{\alpha p, \alpha' p'}^{\mathbf{nn}'} (\mathbf{n}' + \mathbf{x}_{p'} - \mathbf{n} - \mathbf{x}_p)_{\beta},$$

$$A_{\alpha p, \alpha' p'}^{(2)\beta\gamma} = \sum_{\mathbf{n}'} \Phi_{\alpha p, \alpha' p'}^{\mathbf{nn}'} (\mathbf{n}' + \mathbf{x}_{p'} - \mathbf{n} - \mathbf{x}_p)_{\beta} (\mathbf{n}' + \mathbf{x}_{p'} - \mathbf{n} - \mathbf{x}_p)_{\gamma}.$$

Moreover, Born and Huang⁶ established the following properties of this system.³⁾ The solution of (7) is an arbitrary vector that is independent of p :

$$U_{\alpha p}^{(0)} = w_{\alpha}. \quad (10)$$

The consistency condition for the higher-order iterations is that the right-hand sides of the corresponding equations are orthogonal to any such vector. The consistency condition of (8) for $\mathbf{U}_p^{(1)}$ is satisfied automatically because of the particular properties of the matrix $\hat{A}^{(1)}$. Its solution is

$$U_{\alpha p}^{(1)} = - \sum_{p''} \Gamma_{\alpha p, \alpha' p''} A_{\alpha' p'', \alpha'' p''}^{(1)\beta} iK_{\beta} w_{\alpha' p''}, \quad (11)$$

where $\hat{\Gamma}$ is a specially defined inverse of the matrix $\hat{A}^{(0)}$. The consistency condition of (9) for $\mathbf{U}_p^{(2)}$ becomes the equation [after the substitution for $\mathbf{U}_p^{(1)}$ from (11)] for the propagation of sound in the approximation of elasticity theory. It has the form

$$\sum_{pp'} \{ \omega^2 m_p \delta_{pp'} \delta_{\alpha\alpha'} - K_{\gamma} K_{\beta} T_{\alpha p, \alpha' p'}^{\gamma\beta} \} w_{\alpha' p'} = 0, \quad (12)$$

$$T_{\alpha p, \alpha' p'}^{\gamma\beta} = A_{\alpha p, \alpha'' p''}^{(1)\gamma} \Gamma_{\alpha'' p'', \alpha''' p'''} \Lambda_{\alpha''' p''', \alpha' p'}^{(1)\beta} + \frac{1}{2} A_{\alpha p, \alpha' p'}^{(2)\beta\gamma}.$$

This concludes the discussion given in Ref. 6. The response

of displacements within the cell to a strain gradient $\mathbf{U}_p^{(2)}$, in which we are interested, can be found from (9). Substituting (10) and (11) in (9), and using the consistency condition (12) for $\mathbf{U}_p^{(2)}$, we have

$$U_{\alpha p}^{(2)} = \sum_{p''} \Gamma_{\alpha p, \alpha' p''} \{ \omega^2 \mu_{p'} \delta_{p' p''} \delta_{\alpha' \alpha''} - K_{\beta} K_{\gamma} T_{\alpha' p'', \alpha'' p'''}^{\beta\gamma} \} w_{\alpha''},$$

$$\hat{T}_{\alpha' p'', \alpha p}^{\beta\gamma} = T_{\alpha' p'', \alpha p}^{\beta\gamma} - s^{-1} \delta_{pp'} \sum_{p'''} T_{\alpha' p'', \alpha p'''}^{\beta\gamma}, \quad (13)$$

$$\mu_p = m_p - M, \quad M = s^{-1} \sum_p m_p,$$

where s is the number of atoms per unit cell.

It is readily verified that, in the space-time representation, relations (11) and (13) assume the form

$$U_{\alpha p}^{(1)} = - \sum_{p''} \Gamma_{\alpha p, \alpha' p''} A_{\alpha' p'', \alpha'' p''}^{(1)\beta} \varepsilon_{\alpha'' \beta}, \quad (14)$$

$$U_{\alpha p}^{(2)} = \sum_{p''} \Gamma_{\alpha p, \alpha' p''} \left\{ T_{\alpha' p'', \alpha'' p'''}^{\beta\gamma} \frac{\partial \varepsilon_{\alpha'' \beta}}{\partial x_{\gamma}} - \frac{\partial^2 w_{\alpha''}}{\partial t^2} \mu_{p'} \delta_{p' p''} \delta_{\alpha' \alpha''} \right\}, \quad (15)$$

where $\varepsilon_{\alpha\beta} = \partial w_{\alpha} / \partial x_{\beta}$ is the unsymmetrized strain tensor. Expression (14) was used in Ref. 6 in the description of the piezoelectric effect. Expression (15) will be used below in the description of the flexoelectric effect.

To conclude this section, we make one further important remark in relation to the range of validity of (14) and (15). In deriving (14), the consistency condition of (8) was satisfied identically, so that (14) can be justifiably used both for static and time-dependent deformation. Equation (9) was used to obtain (15). Its consistency condition (12) is the dispersion relation for acoustic waves in the approximation of the theory of elasticity, so that expressions (13) and (15) were obtained only for ω and K satisfying this dispersion relation. Hence, strictly speaking, expression (15) cannot be used in the case of inhomogeneous static deformation. We shall show in the Appendix that (15) is valid in the static case as well.

4. DIELECTRIC POLARIZATION IN INHOMOGENEOUSLY DEFORMED CRYSTAL LATTICE

In the last section, we found the displacements of the sites of an inhomogeneously deformed crystal lattice from their equilibrium positions in the undeformed lattice. For the microscopic description of the flexoelectric effect, we must now determine the response of the polarization to these displacements. In the general case of a crystal of arbitrary degree of ionicity, this response can be obtained within the framework of the approach employed by Martin⁷ to describe the piezoelectric effect. However, in this paper, we shall confine our microscopic analysis to the approximation of unpolarizable point ions (this was also used in Ref. 4). In our view, this is a useful approach because even this approximation will exhibit all the basic features of the phenomenon whilst, at the same time, the analysis remains simple and lucid.

Let us begin with the dynamic case. We shall find the

polarization response to the strain gradient in the acoustic wave. By definition, the change $\delta\mathbf{P}$ in the polarization is related to the change $\delta\rho$ in the bound charge density by

$$\operatorname{div} \delta\mathbf{P} = -\delta\rho. \quad (16)$$

Let us take the acoustic wave in the crystal in the form given by (6), so that, starting with (16), we can readily obtain the amplitude \mathbf{P}_K of the polarization wave accompanying sound in the form

$$\mathbf{P}_K = \frac{1}{V} \sum_p Q_p \mathbf{U}_p, \quad (17)$$

where Q_p is the charge of the p th atom in the unit cell and v is its volume. It is clear that (16) enables us to determine only the longitudinal part of the polarization. The transverse part of the polarization is defined in the usual way (see, for example, Ref. 9). Using the expression for \mathbf{U}_p obtained in the last section, we can now determine the contributions to the polarization in the lowest orders in Ka . Substituting (10) in (17), we verify that there is no contribution in the zero order (this is the approximation of the theory of elasticity). This means that, in the approximation of the theory of elasticity,⁴⁾ the acoustic wave propagating through the crystal lattice of arbitrary symmetry will not produce a polarization wave. This is a consequence of the fact that the unit cell is electrically neutral. Substituting (11) in (17), we have, in first order in spatial dispersion,

$$(\mathbf{P}_K)_\alpha = -\frac{1}{v} \sum_{p''} Q_p \Gamma_{\alpha p, \alpha' p'} A_{\alpha' p', \alpha'' p''}^{(1)\beta} i K_\beta w_{\alpha''}. \quad (18)$$

This is the result obtained by Born and Huang for the piezoelectric effect in the rigid ion model.⁶ The flexoelectric response appears in the next order in spatial dispersion. Substitution of (13) in (17) yields the following expression for this response in the acoustic wave:

$$\begin{aligned} (\mathbf{P}_K)_\alpha &= \\ &= \frac{1}{v} \sum_{p''} Q_p \Gamma_{\alpha p, \alpha' p'} (\omega^2 \mu_{p'} \delta_{p' p''} \delta_{\alpha' \alpha''} - K_\beta K_\gamma \tilde{T}_{\alpha' p', \alpha'' p''}^{\beta\gamma}) w_{\alpha''}. \end{aligned} \quad (19)$$

Comparison of (19) with (4) gives us the microscopic expression for the phenomenological tensors \hat{f} and $\hat{\mu}$ introduced above:

$$\chi_{\alpha\nu} f_{\nu\beta\gamma\delta} = -\frac{1}{v} \sum_{p''} Q_p \Gamma_{\alpha p, \alpha' p'} \tilde{T}_{\alpha' p', \beta p''}^{\gamma\delta}, \quad (20)$$

$$\chi_{\alpha\beta} \mu_{\beta\gamma} = v^{-1} Q_p \Gamma_{\alpha p, \gamma p'} \mu_{p'}.$$

The tensor $\hat{\mu}$ assumes a particularly simple form in the case of the diatomic crystal with ion masses and charges m_1 , Q and m_2 , $-Q$, respectively:

$$\mu_{\alpha\beta} = \delta_{\alpha\beta} (m_1 - m_2) / 2Q, \quad (21)$$

which follows from (20) when we take into account the obvious expression for the susceptibility (see, for example, Ref. 6):

$$\chi_{\alpha\beta} = v^{-1} Q_p \Gamma_{\alpha p, \beta p'} Q_{p'}.$$

Let us now consider inhomogeneous static deformation, confining our attention to the simplest situation with a constant strain gradient. We shall find the linear response of mean polarization in a crystal of initial volume V to inhomogeneous deformation specified by the unsymmetrized strain tensor

$$\begin{aligned} \varepsilon_{\alpha\beta}(x) &= \varepsilon_{\alpha\beta}(0) + \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_\gamma} x_\gamma, \\ \varepsilon_{\alpha\beta}(0) &= V^{-1} \int_v \varepsilon_{\alpha\beta}(x) d^3x. \end{aligned}$$

According to Ref. 10, the polarization averaged over the crystal is the mean dipole moment density, so that

$$\delta\mathbf{P} = \tilde{V}^{-1} \sum_n Q_p \tilde{\mathbf{R}}_p^n - V^{-1} \sum_n Q_p \mathbf{R}_p^n, \quad (22)$$

where

$$\tilde{V} = \int_v [1 + \varepsilon_{\alpha\alpha}(x)] d^3x$$

is the volume of the deformed crystal, and \mathbf{R}_p^n and $\tilde{\mathbf{R}}_p^n$ are the radius vectors of the lattice sites before and after deformation, where

$$\begin{aligned} \tilde{\mathbf{R}}_{\alpha p}^n &= \mathbf{R}_{\alpha p}^n + \varepsilon_{\alpha\beta}(0) \mathbf{R}_{\beta p}^n \\ &+ \frac{1}{2} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_\gamma} \mathbf{R}_{\beta p}^n \mathbf{R}_{\gamma p}^n + U_{\alpha p}^{(4)} + U_{\alpha p}^{(2)} + \dots \end{aligned} \quad (23)$$

The second and third terms in this expression represent the displacements of sites in the approximation of the theory of elasticity. The fourth and fifth terms are the contributions to the displacements in the first and second orders in spatial dispersion, which are given by (14) and (15). Using (22) and (23), we finally obtain the expression for $\delta\mathbf{P}$:

$$\begin{aligned} \delta P_\alpha &= \varepsilon_{\alpha\beta}(0) P_\beta^0 - \varepsilon_{\beta\beta}(0) P_\alpha^0 + V^{-1} \sum_n Q_p U_{\alpha p}^{(1)} \\ &+ \frac{1}{6} Q_{\beta\gamma} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_\gamma} + \frac{I}{2} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_\beta} + V^{-1} \sum_n Q_p U_{\alpha p}^{(2)} + \dots, \end{aligned} \quad (24)$$

where

$$\begin{aligned} P^0 &= V^{-1} \sum_{n,p} Q_p \mathbf{R}_p^n, \quad I = V^{-1} \sum_{n,p} Q_p (\mathbf{R}_p^n)^2, \\ Q_{\alpha\beta} &= V^{-1} \sum_{n,p} Q_p [3R_{\alpha p}^n R_{\beta p}^n - \delta_{\alpha\beta} (\mathbf{R}_p^n)^2], \end{aligned} \quad (25)$$

in which P_α^0 and $Q_{\alpha\beta}$ are the mean dipole- and quadrupole-moment densities of the charge distribution in the undeformed crystal. The first three terms in (24) correspond to the response of the mean polarization of the crystal to the deformation, and the last three to the response to the gradient. From the standpoint of flexoelectric effects, we are only interested in the last three terms, but we shall see below that the correct interpretation of these terms will be based on the correct interpretation of the first three "piezoelectric" terms. There appears to be no published work containing the correct interpretation of the piezoelectric effect in this for-

mulation of the problem. We shall therefore begin with an analysis of the piezoelectric contribution.

Expressions similar to the first three terms in (24) were previously encountered in the literature, for example, in the book by Born and Huang⁶ and in Martin's paper.⁷ It was considered in these publications that the first and second terms were nonzero only in pyroelectrics, with \mathbf{P}^0 understood to be a constant of the medium, i.e., the spontaneous polarization of the pyroelectric material. Roughly speaking, the first term was due to the change in the dipole moment vector of the unit cell and the second was obviously a consequence of the change in its volume. Despite its physical attraction, this interpretation cannot be regarded as satisfactory. In fact, according to (25), \mathbf{P}^0 is the mean dipole moment density evaluated over the entire crystal, i.e., it is the ratio of its total dipole moment to its volume. However, it is well-known¹⁰ that the total dipole moment of the crystal may depend on its boundary, and may be different from zero for a crystal of any symmetry. Hence, it is clear that \mathbf{P}^0 is unrelated to spontaneous polarization, and is in the first instance determined by the surface structure of the crystal.

However, the definition of the piezoelectric effect in crystal physics is constructed so that these terms do not contribute. According to the classic textbook on crystal physics by Nye,¹¹ the piezoelectric effect is not the change but the appearance of polarization in response to mechanical stress, i.e., the appearance of a dipole moment in a crystal whose initial dipole moment was reduced to zero by the presence of free charges deposited on its surface (for example, from the ambient atmosphere). The product VP^0 must then be understood [in view of the derivation of (24)] to be the total dipole moment of all the charges in the crystal, including the free charges deposited on the surface. The definition of the piezoelectric effect is thus devised so that \mathbf{P}^0 must be regarded as identically zero, and the first two terms in (24) do not contribute to the effect. Since all standard methods of investigating the piezoelectric modulus in the spatially homogeneous problem correspond to the definition of the piezoelectric effect as given in crystal physics, the terms noted above are not seen experimentally. The piezoelectric effect is thus described by only the third term in (24). When the expression for $\mathbf{U}^{(1)}$ given by (14) is taken into account, this term corresponds to the result that follows from the long-wave method, i.e., (18). More precisely, this correspondence obtains only to within the order of magnitude of the ratio of the volume of the surface layer in which (14) is incorrect to the volume of the entire crystal. To this precision, the piezoelectric modulus is independent of the properties of the surface, and is the same in static and dynamic cases. To conclude our interpretation of the piezoelectric contribution, we note that, both in the static spatially homogeneous and "acoustic" cases, the entire above contribution appears only in the first order in spatial dispersion. The contribution that arises in the approximation of the theory of elasticity turns out to be fictitious. The analysis of the fourth, fifth, and sixth terms in (24) will now be carried out by analogy with the analysis of the piezoelectric terms.

We begin with terms that arise in the approximation of the theory of elasticity, i.e., the fourth and fifth terms in (24).

If we use the considerations employed above in the analysis of the first two terms in (24), $Q_{\alpha\beta}$ and I will not be equal to the corresponding averages evaluated over the unit cell, but will, in fact, be the averages over the entire volume of the crystal. It is readily verified that they are analogous to \mathbf{P}^0 in that they are determined by the structure of the crystal surface. For a correct interpretation of the contribution that we are considering, we must improve the crystal-physics definition of the flexoelectric effect so that it corresponds to the method adopted to measure it in the spatially-homogeneous formulation of the problem. We shall define the flexoelectric effect as the appearance of polarization in an inhomogeneously deformed crystal, which is proportional to the strain gradient when the quadrupole moment of the undeformed crystal is zero. This definition corresponds to the situation where free charges deposited on the surface of the crystal compensate not only the dipole but also the quadrupole moment of the crystal. Compensation of the quadrupole moment is obvious on the basis of energy considerations, and has also been frequently verified experimentally (see, for example, Ref. 12). Thus, if we use our definition, we must set $Q_{\alpha\beta} = 0$, so that the fourth term in (24) does not contribute to the effect. At the analogous stage in the analysis of the piezoelectric effect, there were no contributions due to the surface. In the case of the flexoelectric effect, on the other hand, there remains the term containing I , since the above considerations do not allow us to set I equal to zero. The point is that the requirement that $Q_{\alpha\beta} = 0$ corresponds to the requirement that the quadrupole component of the field around the crystal must be zero. On the other hand, the distribution of charges for which $Q_{\alpha\beta} = 0$ but $I \neq 0$ does not produce a field around the crystal in the quadrupole approximation. It is also clear that compensation of the multipole field component should not, in general, lead to the vanishing of I , since the higher multipole moments correspond to the expansion of the angular dependence of the charge density in terms of higher-order spherical functions,¹³ whereas I is the projection onto the zero-order Legendre polynomial orthogonal to them. The net result is that, using (24) and (15), we can write the flexoelectric contribution to polarization in the form

$$\delta P_{\alpha}^{\text{flex}} = \frac{I}{2} \frac{\partial \varepsilon_{\alpha\beta}}{\partial x_{\beta}} + \frac{1}{v} \sum_{p''} Q_p \Gamma_{\alpha p, \alpha' p'} \tilde{T}_{\alpha' p', \alpha'' p''}^{\beta \gamma} \frac{\partial \varepsilon_{\alpha'' \beta}}{\partial x_{\gamma}}, \quad (26)$$

where \tilde{T} is defined by analogy with I except that, when the sum is evaluated, we have to take into account all the charges in the original crystal, including surface charges which ensure that the macroscopic electric field is zero both inside and outside the crystal. This formula is valid to within a quantity of the order of the ratio of the volume of the surface layer in which (15) is incorrect to the volume of the entire crystal.

Comparing (26) with the flexoelectric response (19) obtained for an acoustic wave, we see that only the last two terms of the equations are the same. These are the contributions of the bulk static flexoelectric effect. In accordance with the phenomenological analysis, the dynamic flexoelectric effect [first term in (19)] does not appear in statics. However, in statics, there is a new term in the case of the bounded

crystal, namely, the first term in (26). It involves the quantity \bar{I} , where \bar{I} itself depends on I and on the disposition on the surface of the initial crystal of the charges responsible for compensating its multipole moments. It is clear from (25) that I is also a function of the structure of the crystal surface. The quantity \bar{I} and, with it, the entire contribution corresponding to the first term in (26) are thus exceedingly sensitive to the surface properties of the crystal. We can therefore call this the surface flexoelectric effect.⁵⁾ Simple estimates show that $\bar{I} \sim e/a$. Since $f \sim e/a$, we see that the contribution of the surface flexoelectric effect is of the same order as the bulk contribution in ordinary dielectrics [cf. (20) and (26)].

To conclude this section, let us try to elucidate qualitatively the origin of the above contribution to the flexoelectric effect.

The static bulk flexoelectric contribution is due to the fact that the lattice that has been inhomogeneously deformed in accordance with the laws of the theory of elasticity is not in equilibrium from the point of view of displacements within the unit cell. It is the displacements that are necessary for true equilibrium that give rise to this contribution to the effect. There is an analogy here with the piezoelectric effect; a piezoelectric regarded as uniformly deformed in the approximation of the theory of elasticity [see (23)] is not in equilibrium from the standpoint of polar optical displacements, whereas a crystal in which each atom is a center of inversion is in true equilibrium under this deformation, and in this case the piezoelectric effect occurs in the former.

The dynamic contribution to the effect will formally vanish when the masses of the atoms in the unit cell are equal [cf. (20) and (21)], and it may then be shown that the effect is due to the nonuniform mass distribution among the cell charges. It is clear that this nonuniformity will not manifest itself in statics, but will lead to additional deviations from the approximation of the theory of elasticity in the dynamic case.

Before we proceed to the interpretation of the surface contribution to the flexoelectric effect, let us elucidate the physical significance of \bar{I} . It follows from the definition that \bar{I} is the mean density of the trace of the quadrupole moment that is defined not in a trace-free manner (see, for example, Ref. 9). It is known that the macroscopic field E does not depend on this quantity,¹³ but it seems to us that the jump in the potential across the boundary of the body does depend upon it. To elucidate this, let us suppose, to begin with, that \bar{I} corresponds to a constant trace density inside the body. It is then readily verified that the potential produced by this density is

$$\varphi(x) = \frac{\bar{I}}{2} \int_V d^3x' \frac{\partial^2}{\partial x_\alpha^2} \frac{1}{|x-x'|} = -2\pi\bar{I} \int_V d^3x' \delta(x-x').$$

Hence, it follows that the jump in the potential across the surface is equal to $2\pi\bar{I}$. Strictly speaking, additional justification is necessary before this result can be used for a crystal. However, it is known that the potential distribution obtained in the analogous approximation for the quadrupole-moment component producing the macroscopic field is in reasonable agreement with experiment (see, for example, Ref. 12). This

enables us to consider that the proportionality between I and the jump in the potential across the surface will also occur in the case of the discrete charge distribution. It is clear that, in a real crystal, this jump occurs across the electric double layer of atomic dimensions.⁶⁾ This type of layer can be formed during the compensation of the multipole moments of the crystal by surface charges.

The surface flexoelectric effect is expressed in terms of \bar{I} , so that we assume that it is due to the above electric double layer. The origin of this effect can be explained as follows. In the initial crystal, all the multipole moments of the double layer are zero, and its only macroscopic parameter is the scalar magnitude of the jump across it, which is proportional to \bar{I} . Under uniform strain, the layer acquires mean (but only even) multipole moments because an odd-rank tensor cannot be constructed from the strain tensor and \bar{I} . Odd moments will also appear under inhomogeneous deformation, including polarization proportional to the strain gradient. This, in fact, constitutes the flexoelectric effect.

5. DISCUSSION OF RESULTS

As indicated above, there is particular interest in the flexoelectric effect in nonpiezoelectric crystals. Let us examine the consequences of the results obtained in this paper from the point of view of the polarization response to the strain gradient in such crystals. We begin with an ordinary dielectric and an intrinsic ferroelectric.

Summarizing our results, we note that, in a crystal whose bulk symmetry does not allow the piezoelectric interaction, the appearance of polarization proportional to the strain gradient can be due to four mechanisms of different physical origin, namely: (1) the bulk static flexoelectric effect, (2) the bulk dynamic flexoelectric effect, (3) the surface flexoelectric effect, and (4) the surface piezoelectric effect. The first three mechanisms have already been discussed in detail, and it has been noted that, in an ordinary dielectric, the contributions of these mechanisms are, generally speaking, of the same order. Let us therefore examine the fourth contribution and show that it can be of the order of the first three in the case of an ordinary dielectric.

In a nonpiezoelectric material, the contribution to polarization, which appears in the first order in spatial dispersion and governs the piezoelectric effect, is zero only in the interior of the specimen. Near the surface, the lattice is distorted and the above contribution may appear in the distorted surface layer. It is clear that surface piezoelectric properties must depend on the structure of the surface and the crystallographic orientation of the crystal faces (a discussion of the analogous problems for ferroelectrics can be found in the paper by Levanyuk and Minyukov¹⁴), and, in particular, they may be different on opposite faces of the specimen. In this situation, surface effects in the spatially inhomogeneous experimental scheme can simulate not only the response, even if small, to the bulk strain, but also the response to the bulk strain gradient. Let us elucidate this by considering an example. Suppose that we have a dielectric plate, and the response to the strain gradient is orthogonal to a pair of plate faces. Suppose further that the piezoelectric moduli in the

surface layers are λ_1 and λ_2 , where λ_1 corresponds to the layer with the greater strain. It is readily verified that, in this situation, the mean piezoelectric modulus must be incremented by an amount of the order of $(\lambda_1 + \lambda_2)d/L$, where d is the thickness of the distorted surface layer and L the thickness of the plate, and there is also an increment to the mean flexoelectric coefficient of the order of $(\lambda_1 - \lambda_2)d$. Using the estimated piezoelectric moduli ($\lambda_1 \simeq \lambda_2 \simeq e/a^2$), and assuming that the scale d is determined by the characteristic interatomic separation a , we see that, in an ordinary dielectric, the contribution of the surface piezoelectric effect to the average flexoelectric coefficient is of the order of e/a , i.e., it is of the same order as the contribution of the bulk flexoelectric effect.

We shall now analyze the polarization response to the strain gradient in the centrally symmetric paraphase of a ferroelectric. As we pass from an ordinary dielectric to a ferroelectric, the order-of-magnitude estimates of the contributions of the above four mechanisms are found to change in a different way. The two bulk contributions exhibit an anomaly at the phase-transition point, and the order-of-magnitude estimates obtained for them are greater by a factor of approximately χ than for ordinary dielectrics. This can be verified by analyzing both the phenomenological relation (4) and the microscopic expression (19). The surface flexoelectric contribution shows no anomaly at the phase-transition temperature and the corresponding order-of-magnitude estimates for a ferroelectric and ordinary dielectric should not, in general, be different. This follows from the fact that \tilde{I} , which appears in these estimates [see (25)], is unrelated to any of the dynamic lattice parameters and should not be sensitive to the ferroelectric properties of the crystal. A universal estimate of the order of magnitude and of the temperature dependence cannot be made for the last contribution, i.e., the contribution due to the surface piezoelectric effect. This is so because the surface piezoelectric effect itself is very sensitive to the orientation of the crystal faces, the state of the surface from the standpoint of the surface phase transition, and a number of other factors.¹⁴ The analysis of this contribution may form the subject of a separate paper. Here, we merely note that the contribution of the surface piezoelectric effect to the polarization response to the strain gradient in a ferroelectric may exhibit an anomaly. This possibility is physically related to the fact that the characteristic width of the distorted surface layer in a ferroelectric may be determined not by the size of the characteristic atomic separation, but by the bulk value of the correlation radius.¹⁴ The temperature anomaly in the piezoelectric moduli of this layer may also lead to an anomaly in the above contribution.

Let us now examine possible experimental observations of the flexoelectric effect. We begin with the dynamic case of a propagating acoustic wave. The effect gives rise to a polarization wave that accompanies the acoustic wave in the piezoelectric crystal. When the polarization wave is longitudinal, the acoustic wave is accompanied by a macroscopic longitudinal electromagnetic wave. The above order-of-magnitude estimates correspond to an electric-field wave with an amplitude of the order of a few volts per centimeter in the case of ultrasound with wavelength in the micron

range and strain-tensor amplitude of the order of 10^{-5} . Since electric induction does not change during the propagation of sound, the estimated amplitude of the accompanying field is the same for both ferroelectrics and ordinary dielectrics. Another manifestation of the flexoelectric effect in the dynamic case is the relative displacement of the soft mode and the transverse acoustic branches in the ferroelectric. A theoretical description of the phenomenon and an analysis of the corresponding experimental situation can be found in the book by Vaks.⁸ We note that, in the "acoustic" situation, the static and dynamic bulk mechanisms contribute to the effect, generally to the same extent, and are indistinguishable in the dynamic experiment. The separation of the two contributions necessitates a separate determination of the static bulk contribution from static measurements.

In the static spatially inhomogeneous formulation of the experiment, the effect includes the following contributions: static bulk, surface flexoelectric, and surface piezoelectric. In ordinary dielectrics, these three contributions are comparable, so that the experimental values of the flexoelectric coefficients obtained in this situation may depend on specimen boundaries, the geometry of the experiment, and the quality of the crystal surfaces. This is the main clue for the experimenter. The most interesting situation from the point of view of the flexoelectric effect in the static spatially inhomogeneous formulation of the problem occurs in ferroelectrics. Firstly, in this formulation, we can directly measure the magnitude of the resulting polarization in zero electric field, so that the effect is several orders of magnitude greater in ferroelectrics than in ordinary dielectrics. Secondly, in this formulation of the problem, the effect in ferroelectrics will be due to, at most, two mechanisms, namely, the static bulk mechanism and the surface piezoelectric mechanism but, when the object and the experimental setup are suitably chosen, only the static bulk mechanism will provide a contribution. This means that the experimental data can be interpreted more unambiguously. As can be seen, it is precisely in the ferroelectric case that static and dynamic data together provide us with the possibility of separating the different contributions to the effect.

We note that the exceptional sensitivity of the flexoelectric effect to surface properties may be exploited as an effective method of studying surfaces.

As far as we know, there have been no systematic studies of the effect in crystals. A discussion of the first attempts at its experimental investigation can be found in Ref. 4.

In conclusion, let us compare our results with those of Ref. 4. Insofar as the qualitative description of the phenomenon is concerned, our paper contains two new properties of the flexoelectric effect as compared with Ref. 4, namely, the considerable difference between the bulk contributions to the effect in the static and dynamic formulations and the presence of important surface contributions in the static spatially inhomogeneous formulation of the problem. The results obtained in the microscopic description are also appreciably different. The discussion given in Ref. 4 is based on relationships analogous to the fourth and fifth terms in (24), but with the following essential differences. The quantities Q and I are interpreted in Ref. 4 as averages not over the entire

crystal, as in the present paper, but over the unit cell. The contribution obtained in Ref. 4 in this way is then interpreted as the bulk contribution. In our view, these identifications and interpretations are not entirely correct. A detailed discussion relating to this point was given in Section 4 of the present paper in the course of the derivation of (26). Moreover, the fact that the approach used in Ref. 4 in the microscopic description of the phenomenon is not correct is, in our view, indicated by the dependence of the flexoelectric coefficient obtained there on the choice of the unit cell. This dependence can readily be demonstrated if we recall that, according to Ref. 4, the flexoelectric coefficient is proportional to a linear combination of \hat{Q} and I , calculated in the light of the above difference. At the same time, it is clear that \hat{Q} and I determined in this way depend on the choice of the unit cell.

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APPENDIX

The aim of this appendix is to prove the validity of (15) in the case of a static inhomogeneous strain.

It follows from (5) that the condition for static equilibrium of a lattice site, whose position is defined by the radius vector $R_{\alpha p}^n$, is

$$\Phi_{\alpha p, \alpha' p'}^{n n'} = 0. \quad (27)$$

Suppose that the macroscopic strain is given by the unsymmetrized strain tensor $\varepsilon_{\alpha\beta}(x)$, which is a slowly-varying function of position. The problem is to find the displacements of atoms within the cell as slow functions of the coordinates, $U_p(\mathbf{x})$, which, in the sum over displacements, correspond to the theory of elasticity and ensure equilibrium in the lattice, i.e.,

$$r_{\alpha p}^{n'} = \int_0^{R'} \varepsilon_{\alpha\beta}(x) dx_{\beta} + U_{\alpha p}(R'), \quad (28)$$

$$R \equiv R_p^n, \quad R' \equiv R_p^{n'}$$

must satisfy (27). Since only the small differences $|\mathbf{n} - \mathbf{n}'|$ are important in (27), it is convenient to write (28) in the form of an expansion in powers of the vector $\mathbf{X} = \mathbf{R}' - \mathbf{R}$:

$$r_{\alpha p}^{n'} = \int_0^R \varepsilon_{\alpha\beta}(x) dx_{\beta} + \varepsilon_{\alpha\beta}(R) X_{\beta} + \frac{1}{2} \frac{\partial \varepsilon_{\alpha\beta}(R)}{\partial R_{\gamma}} X_{\beta} X_{\gamma} + \dots + U_{\alpha p}(R) + \frac{\partial U_{\alpha p}(R)}{\partial R_{\beta}} X_{\beta} + \dots \quad (29)$$

Substituting this in (27) and evaluating the sum, we obtain the differential equation for $U_p(\mathbf{x})$:

$$\dots + A_{\alpha p, \alpha' p'}^{(1)\beta} \frac{\partial U_{\alpha' p'}}{\partial x_{\beta}} + A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'} = - \sum_{p'} A_{\alpha p, \alpha' p'}^{(1)\beta} \varepsilon_{\alpha' \beta} + \frac{1}{2} \sum_{p'} A_{\alpha p, \alpha' p'}^{(2)\beta\gamma} \frac{\partial \varepsilon_{\alpha' \beta}}{\partial x_{\gamma}} + \dots \quad (30)$$

It is readily verified that, as we depart from the equality sign, the terms decrease as powers of the small parameter $a/l \ll 1$ (l is the characteristic scale of a change in $\varepsilon_{\alpha\beta}$). The solution of (30) will be sought by the method of successive approximations. The first two iterations are

$$A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'}^{(1)} = - \sum_{p'} A_{\alpha p, \alpha' p'}^{(1)\beta} \varepsilon_{\alpha' \beta}, \quad (31)$$

$$A_{\alpha p, \alpha' p'}^{(0)} U_{\alpha' p'}^{(2)} = - A_{\alpha p, \alpha' p'}^{(1)\beta} \frac{\partial U_{\alpha' p'}^{(1)}}{\partial x_{\beta}} + \frac{1}{2} \sum_{p'} A_{\alpha p, \alpha' p'}^{(2)\beta\gamma} \frac{\partial \varepsilon_{\alpha' \beta}}{\partial x_{\gamma}}. \quad (32)$$

The consistency condition for (31) in $U_p^{(1)}$ is identical with the consistency condition for (8), and is satisfied identically, whilst its solution is identical with the result obtained by the method of long waves, i.e., (14). The consistency condition for (32) [after elimination of $U_p^{(1)}$ with the aid of (14)] is the static equation of the theory of elasticity [cf. condition (12)]:

$$\sum_{pp'} T_{\alpha p, \alpha' p'}^{\gamma\beta} \frac{\partial \varepsilon_{\alpha' \beta}}{\partial x_{\beta}} = 0.$$

It is readily verified that the solution (32) is identical with the first term in (15), q.e.d.

- ¹ Here and below, we imply summation over all repeating indices.
- ² This property is discussed in the case of the piezoelectric effect in Ref. 5.
- ³ In writing this set of equations, we have used a somewhat different normalization from that adopted in Ref. 6. These properties are therefore not literally the same as in the original text.
- ⁴ According to (10) and (6), this approximation corresponds to the acoustic wave in which lattice-site displacements depend on the number of the atom in the unit cell only through the phase factor $\exp[i\mathbf{k} \cdot (\mathbf{kn} + \mathbf{x}_p)]$, i.e., the wave propagates as in an elastic continuous medium. In this sense, the wave will be referred to as an acoustic wave in the approximation of the theory of elasticity.
- ⁵ It is clear that we cannot, within the framework of this scheme, provide a quantitative description of the surface flexoelectric effect, but it seems that the order-of-magnitude estimate of the effect obtained in this scheme should be correct.
- ⁶ We note that a constant jump across an arbitrary segment of the surface is also a consequence of the fact that the macroscopic field is zero around and inside the initial crystal.

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